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(71) Applicants
Shiseido Company Ltd.,
No. 7-5-5, Ginza Chuo-ku,
Tokyo, Japan
(72) Inventors
Shigenori Kumagai
Michiko Nara
(74) Agents
Marks & Clerk

(54) **A gel composition**

(57) A gel composition comprises an organically modified or unmodified montmorillonite series clay mineral and a liquid crystal comprising a surfactant-water system compounded in an organic solvent. The gel composition can be used in cosmetic compositions.

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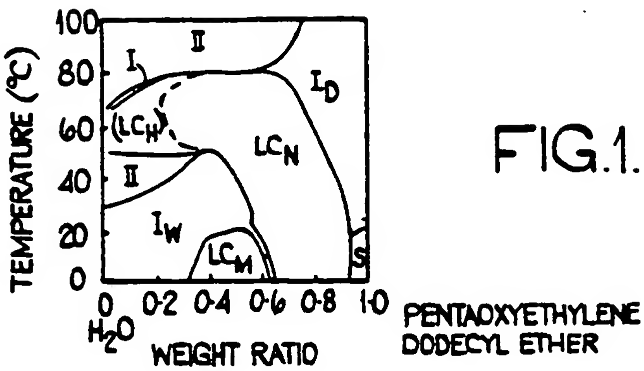


FIG.1.

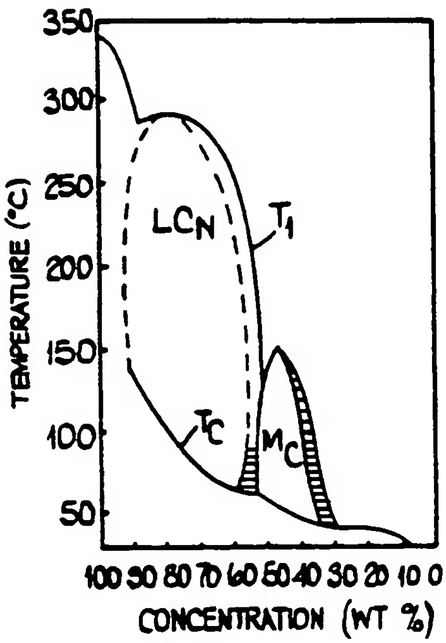
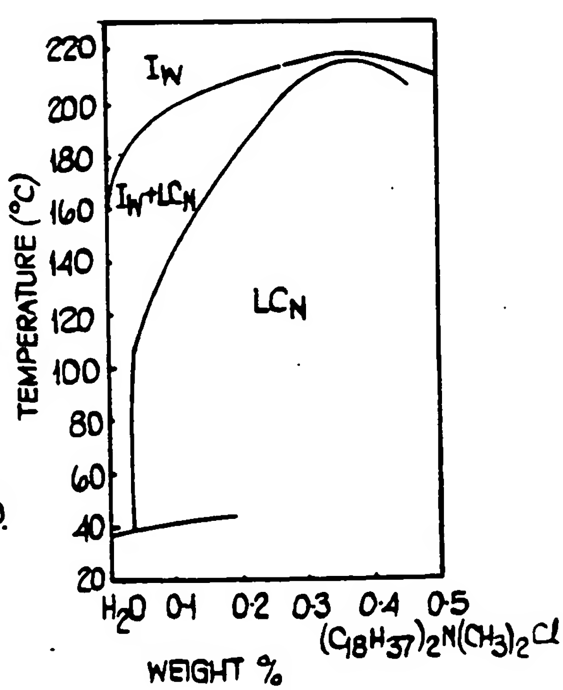


FIG.2.

FIG.3.



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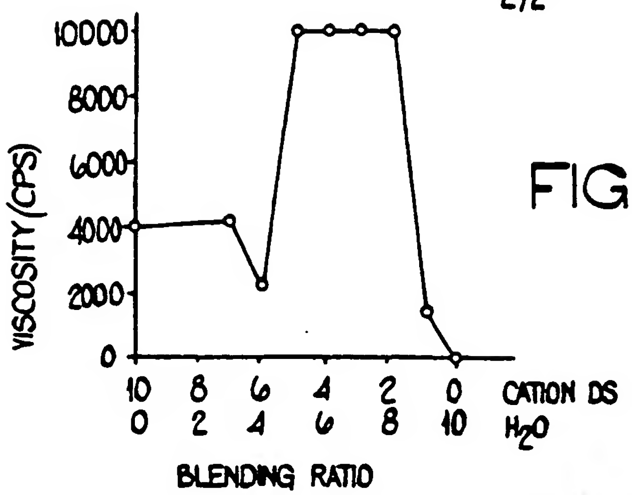
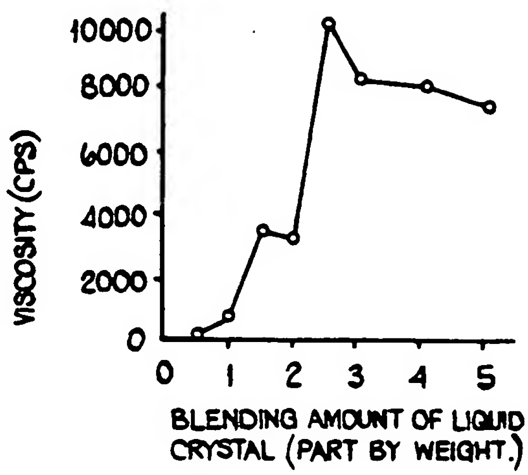


FIG.4.

FIG.5



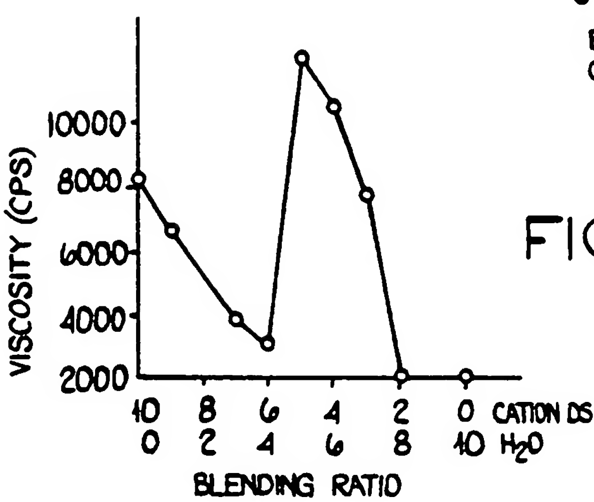
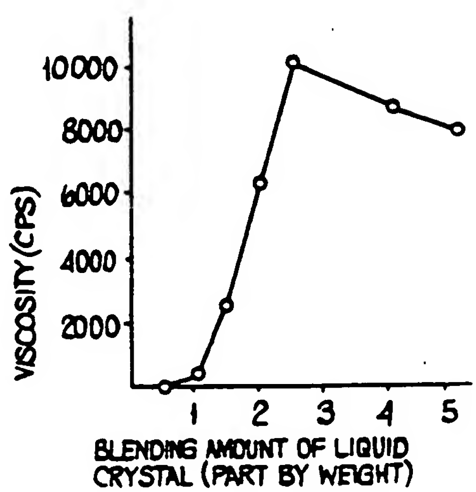


FIG.6.

FIG.7.



SPECIFICATION

A gel composition

This invention relates to a gel composition comprising a montmorilonite series clay mineral, and to a cosmetic composition prepared using said gel composition.

A montmorilonite series clay mineral is a naturally occurring colloidal aluminum silicate hydrate, known as a main ingredient of bentonite, and is generally represented by the structural formula:

$$(X, Y)_{2-3}(Si, Al)_4O_{10}(OH)_2Z_{1/3}.nH_2O$$

wherein X = Al, Fe (III), Mn (III) or Cr (III); Y = Mg, Fe (II), Mn (II), Ni, Zn or Li; and Z = K, Na or Ca. This silicate exhibits such a strong hydrophilicity that it absorbs a large amount of water between lattice planes thereof and greatly swells to form a gel having a high structural viscosity.

It has been known that this montmorilonite series clay mineral can be made oleophilic and can be converted to a thickening agent for organic solvents by replacing water or exchangeable cations existing between its lattice planes with an organic polar compound or organic cation (see Jordan, J. W., *J. Phys. and Colloid Chem.*, *53*, 294 (1949); Jordan, J. W., et al., *ibid.*, *54*, 1196 (1950); Jordan, J. W., et al., *Kolloid-Z.*, *137*, 40 (1954), etc.). The thus-modified material is generally called "organically modified montmorilonite", and has been used to prevent precipitation of pigments in paints, printing inks, cosmetics, etc., or improve the rheological characteristics thereof. In such cases, mechanical energy, suitable temperature and suitable additives are necessary to permit the organically modified montmorilonite to swell more effectively. As the suitable additives, there are known methanol, ethanol, acetone, propylene carbonate, etc. However, these additives are not desirable for cosmetic use in view of their influence on the human body, their boiling point and stability. U.S. Patents 2,531,427 and 3,422,185, both teach the use of organically modified montmorilonites in cosmetics.

Cosmetics are roughly classified into liquid type, cream type, wax type, granular type and aerosol type from the standpoint of form used. Of these, in the liquid type and cream type cosmetics, a gelling agent is often blended therein to improve the application feeling and fluidity and to prevent precipitation of pigments. It has been known to use as an oil-type gelling agent, aluminum soap, oil-soluble cellulose derivatives, organically modified montmorilonite and the like. Of these, the organically modified montmorilonite is superior in thixotropy which is an important property in gellation. Thus, the organically modified montmorilonite has been widely used as an indispensable ingredient in oil-type eye liners, eye shadows, mascaras and rouges and in nail enamels. Furthermore, the organically modified montmorilonite has also been often used in emulsion-type foundations and creams.

As a result of investigations into new additives to replace the above-described known additives for organically modified montmorilonites, it has been discovered that a mixture of suitable surfactant and water in a certain mixing proportion is extremely effective. The mixing proportion of the suitable surfactant to water is such that the surfactant-water system forms a liquid crystal of lamellar structure (a so-called "neat phase" results). A neat phase is observed with either nonionic surfactants or ionic surfactants. Figures 1 and 2 each show the phase diagram of a pentaoxyethylene dodecyl ether-water system or a sodium laurate-water system, the region indicated by LC_N is the region of a neat phase forming a lamellar structure. The phase diagram of a dioctadecyldimethylammonium chloride-water system is shown in Figure 3. The latter system is characterized in that the region where the liquid crystal is in a lamellar structure is extremely large.

It has also been discovered that a good gel can be obtained without conducting organic modification of the montmorilonite by compounding unmodified montmorilonite with a surfactant-water composition forming a liquid crystal of lamellar structure. This gel is obtained without using conventional additives such as ethanol and acetone and without the disadvantages which accompany their use. It had never previously been known to use organically unmodified montmorilonite series clay mineral as a thickening agent of organic solvents, but this has now become possible by compounding the unmodified montmorilonite with a liquid crystal.

Accordingly, the invention resides in a gel composition comprising an organically modified or unmodified montmorilonite series clay mineral and a liquid crystal comprising a surfactant-water system compounded in an organic solvent.

In cosmetics where the montmorilonite-liquid crystal gel composition described in the preceding paragraph is employed, the following advantages can be obtained:

(1) By selecting the surfactant-water liquid crystal so as to meet the preparation conditions (e.g., temperature), this can give rise to the highest gellation property, whereby a stable viscosity behaviour is obtained.

(2) It is possible to reduce the amount of the organically modified montmorilonite which is present in the conventional cosmetics by about 0.5 to several percent.

(3) It becomes possible to use organically unmodified montmorilonite as an oil-type gellating agent, whereby the preparation cost and stability of products are much improved.

In the accompanying drawings:

Figures 1, 2 and 3 are graphs showing phase diagrams of pentaoxyethylene dodecyl ether, sodium laurate and dioctadecyldimethylammonium chloride in water, respectively, wherein the region indicated by LC_N is of the neat phase forming a lamellar structure.

Figures 4 and 5 are graphs showing the viscosity of the system of low-boiling hydrocarbon, dimethyldioctadecylammonium montmorilonite, cationic surfactant and water.

Figures 6 and 7 are graphs showing the viscosity of the system of low-boiling hydrocarbon, unmodified montmorilonite, cationic surfactant and water.

Additionally, other symbols in the drawings indi-

cate the following:

IW: a region where the surfactant forms micelles and is dissolved in water.

I_D: a region where water is dissolved in the surfactant.

II: a region where a solution wherein a slight amount of the surfactant is dissolved in water and a solution wherein a slight amount of water is dissolved in the surfactant coexist (two-phase).

LC_M: a region where the liquid crystal has a hexagonal structure.

S: a region where the surfactant precipitates as a solid.

As noted above, organically modified montmorilonites have been conventionally used as thickening agents for paints, inks, cosmetics, etc. Organic compounds which can be used for the organic modification of montmorilonite include fatty acid amine salts such as an octadecylamine acetic acid salt ($C_{18}H_{37}NH_2 \cdot HOCOCH_3$), quaternary ammonium salts such as dimethyldialkylammonium chlorides ($R_2N(CH_3)_2 \cdot Cl$), or composite materials thereof. Representative examples of organically modified montmorilonites which can be used in the present invention are Bentone 38 and Bentone 27 (products of National Lead Company modified with quaternary ammonium salts) as disclosed in U.S. Patent 2,432,427, and Orben (a product of Shiraishi Kogyo K.K.) as disclosed in Japanese Patent Publication 3018/58.

The guide line as to the type of surfactants which can make the neat phase present can be roughly explained in terms of "HLB" (hydrophile-lypophile balance). In the case of nonionic surfactants, the neat phase does not appear when the HLB is too high (e.g., about 10 or higher). On the other hand, since the HLB of ionic surfactants does not greatly vary, almost all conventionally employed ionic surfactants appear to be capable of providing the neat phase. Specific examples of surfactants which can be used in the invention will be listed below, however, this list is provided for illustration only and is not meant to limit the scope of the present invention.

(a) Nonionic surfactants: Representative examples include polyoxyethylenealkyl ethers (for example, see F. Harusawa et al., *Colloid & Polymer Sci.*, *252*, 613 (1974)), polyoxyethylenealkylphenyl ethers (for example, see K. Kenjo, *Bull. Chem. Soc. Japan*, *39*, 685 (1966)), polyoxyethylene fatty acid esters, polyoxyethylenesorbitan fatty acid esters, Pluronic type surfactants, sucrose esters, etc.

(b) Anionic surfactants: Representative examples include soaps (for example, see C. Madelmont & R. Perron, *Colloid & Polymer Sci.*, *254*, 581 (1976)), alkyl sulfuric acid salts (for example, see D. G. Rance & S. Friberg, *J. Colloid & Interface Sci.*, *60*, 207 (1977)), alkylaryl sulfonic acid salts, aerosol type surfactants (for example, see J. Rogers & P. A. Winsor, *Nature*, *216*, 477 (1967)), etc.

(c) Cationic surfactants: Representative examples include quaternary ammonium salts (for example, see H. Kunieda & K. Shinoda, *Yukagaku*, *27*, 417 (1978)), etc.

(d) Natural surfactants: Representative examples include phospholipid type surfactants (for example, see M. B. Abramson, *Biochim. Biophys, Octa.*, *225*, 167 (1971)), etc.

(e) Mixture type surfactants: Representative examples include anion-cation surfactants (for example, see D. H. Chen & D. G. Hall, *Kolloid-Zu. Z. Polymere*, *251*, 41 (1973)), etc.

Any organic liquid which is liquid at normal (room) temperature may be used in the present invention. Suitable examples of organic liquids which can be used include vegetable oils, animal oils, mineral oils, aliphatic hydrocarbons which are liquid at normal temperature (e.g., C_4-C_{20} aliphatic hydrocarbons (in a normal state)), aromatic hydrocarbons which are liquid at normal temperature (e.g., benzene, toluene, xylene, etc.), esters which are liquid at normal temperature (e.g., ethyl acetate, butyl acetate, isopropyl myristate, glyceride, etc.), alcohols (e.g., ethanol, isopropanol, butanol, octadodecanol, etc.), silicone oils, and the like.

The gel composition may be prepared by mixing the unmodified or the organically modified montmorilonite, an organic liquid and the liquid crystal at a suitable temperature using a suitable mixer. A suitable proportion of the liquid crystal to the montmorilonite ranges from about 10 to 200% by weight, and particularly preferably from about 30 to 100%. The surfactant and water comprising the liquid crystal may be added separately or the liquid crystal may be previously prepared. However, where an organic solvent in which the liquid crystal will be destroyed is used, the liquid crystal must be previously prepared before the addition. The total amount of the montmorilonite and surfactant-water system in the gel composition is about 0.1 to 30% by weight with the remainder being the organic liquid.

In order to compare gelling ability of conventionally used additives like ethanol with that of the liquid crystal, the viscosities of unmodified and organically modified montmorilonite gels prepared therefrom are tabulated in Table 1. In Table 1, the unmodified montmorilonite was a high purity material, the organically modified montmorilonite used was dimethyldioctadecylammonium montmorilonite, the organic solvent was a low-boiling hydrocarbon, and viscosities of the gel compositions obtained by mixing 5 parts of ethanol or liquid crystal with a suspension of 5 parts of the montmorilonite dispersed in 90 parts of the solvent were measured at 30°C using a model B viscometer.

It is seen from Table 1 that, where the liquid crystal is used, the viscosity of the gel can be controlled as desired by changing the kind of the surfactant or the proportion of the surfactant to water, and that gels with viscosities ranging from a higher level to a lower level than that in the case of using ethanol can be obtained.

It is seen from Table 1 that the composition obtained through gellation of organically unmodified montmorilonite by compounding the liquid crystal showed about the same as or higher viscosity than that of the composition obtained through gellation of the organically modified montmorilonite by compounding ethanol. Thus, it was demonstrated that montmorilonite can be used as a thickening agent of organic solvents without conducting organic modification when a surfactant-water

system is compounded with the montmorilonite.

It is another feature of this invention that, while no gellation takes place at 80°C in the case of ethanol, a good gel can be obtained in the case of the liquid crystal by properly selecting the surfactant.

TABLE 1
Viscosities of Montmorilonite Gel Composition

Clay Mineral	*Additive/Liquid Crystal*	*Dispersing Temperature* (°C)	*Viscosity* (cp)
Dimethyl-dioctadecyl-ammonium montmorilo-nite	Ethanol (95%)	25	5,800
"	"	80	300
"	Tetraoxyethylene dodecyl ether	25	600
"	Tetraoxyethylene dodecyl ether/water (80/20)	25	>10,000
"	" " (60/40)	25	>10,000
"	" " (40/60)	25	5,500
"	" " (20/80)	25	1,500
"	Polyoxyethylenesorbitan monooleate/water (90/10)	25	5,700
"	" " (75/25)	25	1,800
"	Polyoxyethylenesorbitan monostearate/water (75/25)	80	1,900
"	" " (50/50)	80	10,000
"	" " (25/75)	80	1,100
Unmodified montmorilo-nite	Polyoxyethylene dodecyl ether/water (75/25)	25	6,600
"	Acetone	25	<100
"	Ethanol (95%)	25	<100

In order to compare the swelling degree of organically modified montmorilonite, the interplanar distance of the (O, O, I) planes in the organically modified montmorilonite was measured to obtain the results shown in Table 2. Samples were prepared by mixing 30 parts of dimethyldioctadecylammonium montmorilonite with 60 parts of a low-boiling hydrocarbon, ethanol or 10 parts of liquid crystal. It is seen from Table 2 that the liquid crystals widened the interplanar distance.

TABLE 2
Interplanar Distance of Dimethyl-dioctadecylammonium Montmorilonite

Additive/Liquid Crystal	*d (Å)*
Control	24-28
Ethanol (95%)	58
Pentaoxyethylene dodecyl ether/water (80/20)	61
Hexaoxyethylene dodecyl ether/water (70/30)	63
Commercilly available polyoxyethylene dodecyl ether/water (80/20)	68

Figures 4-7 show examples using a liquid crystal of a cationic surfactant (Cation DS, a cationic surfactant made by Sanyo Chemical Industry Company, Ltd.).

Figure 4 is a graph showing the relation between the ratio of the cationic surfactant to water and the viscosity of the system comprising 45 parts of a low-boiling hydrocarbon, 2.5 parts of dimethyldioctadecylammonium montmorilonite and 2.5 parts of the cationic surfactant and water. From Figure 4, it is seen that a good gel can be obtained when the ratio of Cation DS to water is in the range of from 5:5 to 2:8.

Figure 5 is a graph showing the viscosity of a system comprising 2.5 parts of dimethyldioctadecylammonium montmorilonite and 0.5 to 5 parts of liquid crystal (Cation DS:water = 1:1) and being made 50 parts by adding a low-boiling hydrocarbon. It is seen that good gels are formed when the amount of added liquid crystal is 100% or more based on dimethyldioctadecylammonium montmorilonite.

Figure 6 is a graph showing the relation between the ratio of the cationic surfactant to water and the viscosity of the system comprising 45 parts of low-boiling hydrocarbon, 2.5 parts of montmorilonite unmodified and 2.5 parts of the cationic surfactant and water.

Figure 7 is a graph showing the viscosity of the system comprising 2.5 parts of montmorilonite and 0.5 to 5 parts of liquid crystal (Cation DS:water = 1:1) and being made 50 parts by adding a low-boiling hydrocarbon. It is seen that good gels are formed when the amount of added liquid crystal is

about 80% or more based on the montmorilonite.

The gel composition may be mixed with a conventional liquid-, cream-, or oil-type cosmetic as a gelling agent or a thickener to improve the feeling or texture of the composition or to prevent the precipitation of pigments in a manner well known in the art. These compositions may contain ultraviolet ray absorbing agents, antioxidants, corrosion inhibitors, dyes, perfumes, plasticizers, etc. in suitable conventional amounts.

The present invention will now be described in more detail by the following examples.

The gel compositions below were prepared using pentaoxyethylene dodecyl ether as surfactant. In all of the examples described herein, "Veegum HV" (see The Cosmetic, Toiletry and Fragrance Association Inc., Cosmetic Ingredient Dictionary (hereinafter "CTFA-CID")) was used as the unmodified montmorilonite, and all of the organically modified montmorilonites used were those in which Veegum HV was organically modified. The compositions were prepared by merely mixing and stirring the ingredients at room temperature. Unless otherwise indicated, amounts are in parts by weight.

EXAMPLES 1 & 2

	Ex. 1	*Ex. 2*
Isoparaffinic Hydrocarbon (b.p. 173-195°C)	92.5	93.0
Organically Modified Montmorilonite (Dimethyldioctadecyl Ammonium Montmorilonite)	5	—
Unmodified Montmorilonite	—	5
Pentaoxyethylene Dodecyl Ether	2	1.5
Water	0.5	0.5

EXAMPLES 3 & 4

	Ex. 3	*Ex. 4*
Toluene	66	66
Butyl Acetate	25	25
Organically Modified Montmorilonite (Dimethylbenzyldodecyl Ammonium Montmorilonite)	6	—
Unmodified Montmorilonite	—	6
Pentaoxyethylene Dodecyl Ether	2	2
Water	2	2

Even when a surfactant when used alone does not form a liquid crystal with water, such a surfactant may be used by combining it with other surfactants to form a liquid crystal and swell the montmorilonite. Such examples are shown below.

EXAMPLES 5 & 6

	Ex. 5	*Ex. 6*
Squalane	90	90
Sorbitan Monooleate	1	1
Polyoxyethylenesorbitan Monooleate	1	1
Organically Modified Montmorilonite (Dimethyldioctadecyl Ammonium Montmorilonite)	6	—
Unmodified Montmorilonite	—	6
Water	2	2

Examples of cosmetics prepared by applying the gel compositions of the present invention will be described below, in which compounding amounts are in percent by weight.

EXAMPLES 7 TO 10

Mascara Preparation

	Comparative Example	*Example Nos. 7*	*8*	*9*	*10*
Low-boiling Hydrocarbon (b.p. 173-195°C)	56	58	57.5	57	57
Bees Wax	10	10	10	10	10
Microcrystalline Wax	10	10	10	10	10
Organically Modified Montmorilonite (Dimethyldioctadecyl Ammonium Montmorilonite)	2	1	1.5	2	—
Unmodified Montmorilonite	—	—	—	—	2
Ethanol	2	—	—	—	—
Polyoxyethylenesorbitan Monostearate	—	0.25	0.25	0.25	0.5
Purified Water	—	0.75	0.75	0.75	0.5
Pigment (Iron Oxides)	20	20	20	20	20
Perfume	0.05	0.05	0.05	0.05	0.05
Viscosity of Product (cp)	38,000	36,000	45,000	53,000	52,000

With the products gelled with the liquid crystal (Examples 7-10), only about half the amount of the organically modified montmorilonite was necessary to obtain the same viscosity of the product gelled with ethanol (Comparative Example) and, even when the gelled product had a high viscosity, it was quite smoothly usable due to its thixotropic behavior. The stability of the products of Examples 7-10 was better than that obtained by using ethanol.

EXAMPLES 11 & 12

Nail Enamel Preparation

	Ex. 11	*Ex. 12*
Toluene	40	40
Ethyl Acetate	30	30
Nitrocellulose (1/4 second)	10	10
Modified Alkyd Resin	10	10
Plasticizer (Acetyltributyl Citrate)	5	5
Organically Modified Montmorilonite (Dimethylbenzyldodecyl Ammonium Montmorilonite)	2	—
Unmodified Montmorilonite	—	2
Polyoxyethylene Lauryl Ether	0.7	0.7
Purified Water	0.3	0.3
Pearl Essence	1.4	1.4
Pigment (Iron Oxides)	0.5	0.5
Pigment (Titanium Dioxide)	0.1	0.1

It has hitherto been known that the addition of organically modified montmorilonite as a pigment-precipitation preventing agent is indispensable in the preparation of nail enamel. However, the degree of swelling of organically modified montmorilonite varies depending upon the solvent composition, and a sufficient mechanical stirring power is required for gellation. In this respect, when a surfactant-water liquid crystal is used, the swelling of the organically modified montmorilonite is always exhibited to the highest extent, and considerably lower mechanical stirring power is required for gellation.

EXAMPLES 13 & 14

Foundation Preparation

	Ex. 13	*Ex. 14*
Liquid Paraffin (Drakeol 9, see CTFA-CID)	33	33
Solid Paraffin (Ozokerite, see CTFA-CID)	10	10
Organically Modified Montmorilonite (Stearylamide Montmorilonite)	5	—
Unmodified Montmorilonite	—	5
Dimethyldioctadecyl Ammonium Chloride	2	2
Purified Water	40	40
Pigment (Iron Oxides)	5	5
Talc	5	5
Perfume	0.1	0.1
Antiseptic	0.05	0.05

These emulsion systems obtained by gelling the montmorilonite with the liquid crystal showed an extremely excellent stability and, when used, it was not sticky and gave a refreshed feeling.

CLAIMS

1. A gel composition comprising an organically modified or unmodified montmorilonite series clay mineral and a liquid crystal comprising a surfactant-water system compounded in an organic solvent.

2. A gel composition consisting essentially of an organically modified or unmodified montmorilonite series clay mineral and a liquid crystal comprising a surfactant-water system compounded in an organic solvent.

3. A gel composition as claimed in Claim 1, or Claim 2 wherein said liquid crystal has a lamellar structure.

4. A gel composition as claimed in any one of Claims 1 to 3, wherein the compounding ratio of said organically modified or unmodified montmorilonite series clay mineral to said liquid crystal is in the range of from about 1:0.1 to 1:2 by weight.

5. A gel composition substantially as hereinbefore described with reference to the examples and the accompanying drawings.

6. A cosmetic composition including a gel composition comprising an organic solvent, an organically modified or unmodified montmorilonite series clay mineral and a liquid crystal comprising a surfactant-water system.

7. A cosmetic composition including a gel composition as claimed in any one of Claims 1 to 5.

8. A cosmetic composition substantially as hereinbefore described with reference to the examples.

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